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DFT studies on hexaborate(2-) and heptaborate(2-) anions

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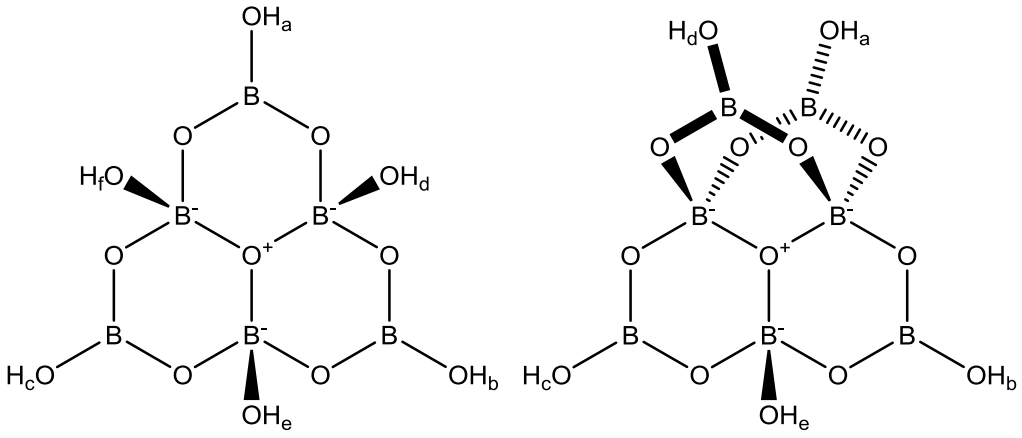
GRAPHICAL ABSTRACT



Abstract *Bond counting rules allow chemists to unearth low-energy structures by sequentially sieving undesirable interactions whilst maximizing stabilizing interactions. The approach is applied to model hydrogen-bonding in polyborate anions.*

Keywords Polyborate anions; hydrogen bonding; polyhydroxybenzoquinones

INTRODUCTION

Conformational analysis is a painstaking task even with advances in computing power. Bond counting rules (BCR) have been used to identify low-energy structures for B/C/N superhard materials,[1,2] and doped fullerenes,[3] based upon observations[4] that stable structures had no B-B nor N-N bonds, whilst the number of C-C and B-N bonds were maximized. The BCR works well for B/C/N systems due to the large energetic differences (*ca.* 100-200 kJ mol^{-1}) between the weakest and strongest covalent bonds. It should be possible to extend BCRs to hydrogen-bonded systems,[5,6] as typical hydrogen-bond energies (*ca.* 20 kJ mol^{-1}) are far greater than either thermal energy or computational error.

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Polyborate anions can form a myriad of structures including isolated rings or cages, 1-D chains, 2-D sheets and 3-D networks due to corner sharing linked triangular BO_3 and tetrahedral BO_4 units.[7-11]

RESULTS AND DISCUSSION

Computational Methodology

Gas-phase B3LYP/6-311++G(*d*,*p*) DFT calculations were performed using *Gaussian09*.[12]

Hexaborate

The $[B_6O_7(OH)_6]^{2-}$ anion consists of BO_3 triangles (Δ) & BO_4 tetrahedra (T) linked by vertices and a central 3-coordinate O atom to form three 6-membered rings containing 3- and 4-coordinate borons (Figure 1a) with a Christ and Clark description of 6:3Δ + 3T.[7] The calculations suggest that *exo* OH groups attached to tetrahedral borons will preferentially orientate *anti*- to the ring B-O bonds. The most stable structures (Figure 2a) possess an unbroken, quasi-triangular cyclic network ($r_{O\text{-}H}$ = 0.967 Å; $r_{O\cdots H}$ = 2.25 Å; $\angle_{O\text{-}H\cdots O}$ = 135.7 °; $r_{O\cdots O}$ = 3.02 Å) of cooperative intramolecular hydrogen bonds (IHBs). The cyclic network maximizes the number of stabilizing interactions in complete accord with bond counting rule approaches. Breaking an IHBs (so that two remain) *via* B-O bond rotation, raises the conformational energy by *ca.* 15 kJ mol^{-1} (Table 1), which is consistent with hydrogen bond energies.[6] In complete contrast, rotation of the planar hydroxyl groups attached to a trigonal boron atom has a negligible energetic effect due to absence of H-bonding (no bond critical point) coupled with almost identical electrostatic attractions between the electropositive hydrogen of the OH group and the electronegative ring O atoms.

QTAIM analyses (Figure 2a) confirm the covalent nature of the OH groups with large ρ_{BCP} and -ve ∇^2 values (*ca.* 0.36 a.u. and -2.40 a.u. respectively). The closed-shell IHBs have much smaller ρ_{BCP} and ∇^2 values (*ca.* 0.02 a.u. and 0.05 a.u. respectively) reflecting their weaker nature. A 0.007 a.u. reduction in ρ_{BCP}, a 0.006 Å elongation in r_{OH} and a *ca.* 100 cm^{-1} red shift in ν_{OH} are observed for *exo vs* planar OH groups, reflecting the loss in electron density that occurs during hydrogen bond formation.

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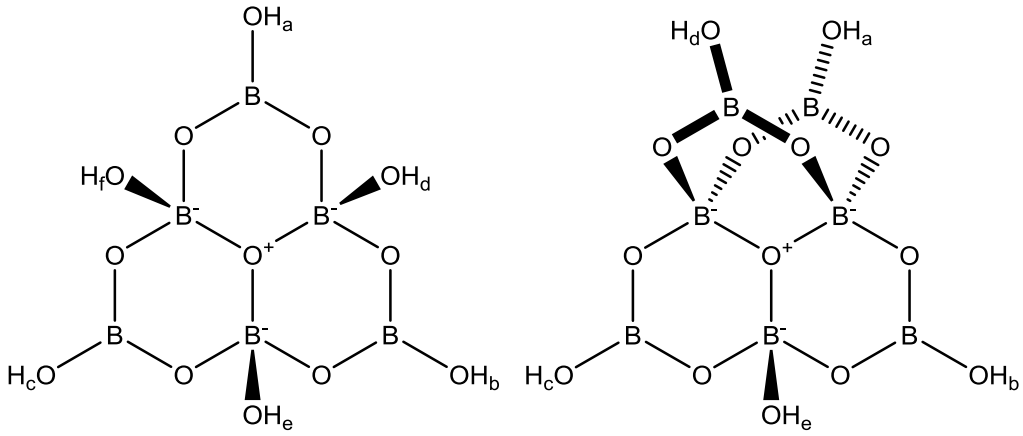
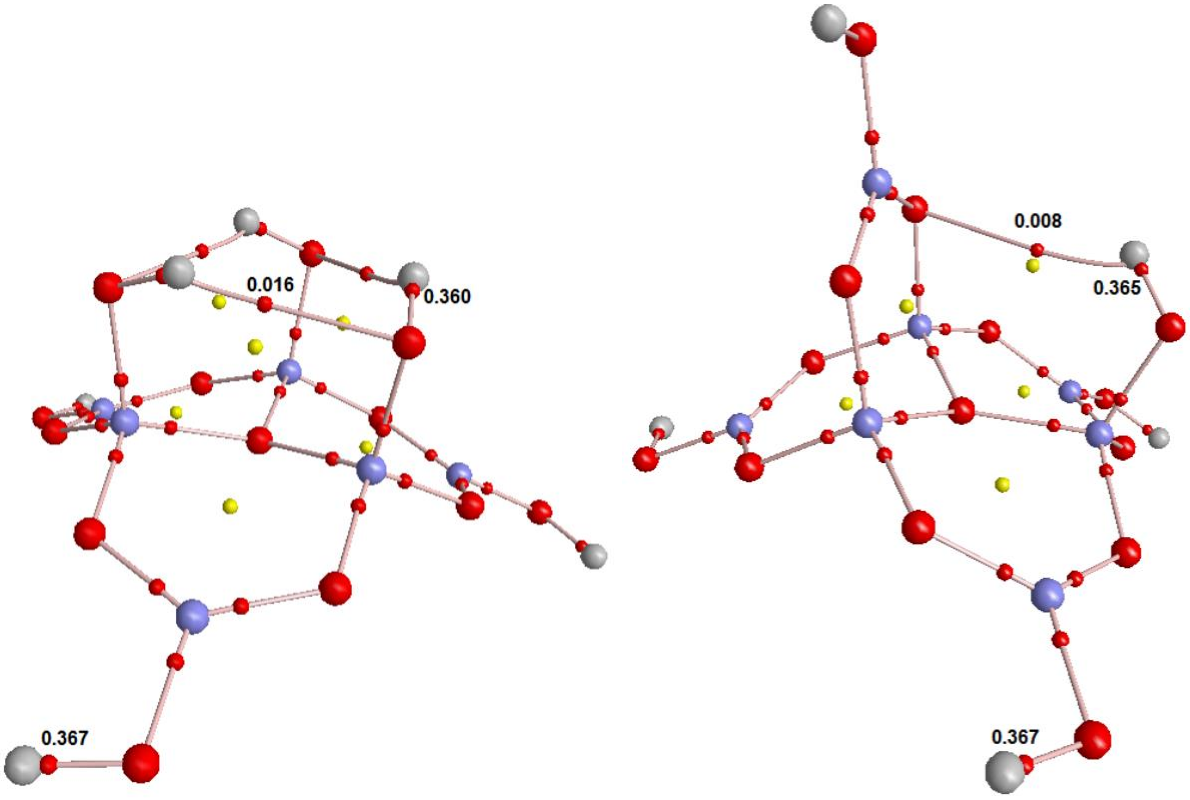


(a) (b)

Figure 1 Polyborate anion skeletal structures: (a) $[B_6O_7(OH)_6]^{2-}$; (b) $[B_7O_9(OH)_5]^{2-}$



(a) (b)

Figure 2 QTAIM bond graph (AIM2000) and selected ρ_{BCP} values (a.u.): (a) $[B_6O_7(OH)_6]^{2-}$; (b) $[B_7O_9(OH)_5]^{2-}$. Small red and yellow dots represent bond and ring critical points respectively.

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Table 1 Gas phase B3LYP/6-311++G(*d*,*p*) relative energies (kJ mol^{-1}) for the $[B_6O_7(OH)_6]^{2-}$ hexaborate anion. Initial hydrogen atom orientations C = clockwise, A = anticlockwise and sites (a-f) relative to Figure 1a. Sixty four (2^6) different combinations were generated giving rise to twelve unique enumerations.

Outer (Trigonal) OH groups			Inner (Tetrahedral) OH groups			ΔE (kJ mol^{-1})
a	b	c	d	e	f	
C	C	C	A	A	A	0
C	C	C	C	C	C	0
C	C	A	A	A	A	1
C	C	A	C	C	C	1
C	C	A	A	A	C	14
C	C	A	C	C	A	14
C	C	C	C	A	A	15
C	C	C	C	C	A	16
C	C	A	C	A	A	16
C	C	A	A	C	C	17
C	C	A	A	C	A	18
C	C	A	C	A	C	19

Table 2 Gas phase B3LYP/6-311++G(*d*,*p*) relative energies (kJ mol^{-1}) for the $[B_7O_9(OH)_5]^{2-}$ heptaborate anion. Initial hydrogen atom orientations C = clockwise, A = anticlockwise and sites (a-e) relative to Figure 1b. Thirty two (2^5) different combinations were generated giving rise to sixteen unique enumerations.

OH groups					ΔE (kJ mol^{-1})
a	b	c	d	e	
C	C	C	C	C	0
C	A	C	A	A	0
C	A	A	C	A	1
C	A	C	A	C	1
C	A	A	C	C	1
C	C	C	C	A	1
C	C	A	A	A	1
C	C	A	A	C	2
C	C	C	A	A	2
C	A	A	A	A	2
C	C	A	C	A	2
C	A	A	A	C	2
C	C	A	C	C	3
C	C	C	A	C	3
C	A	C	C	C	3
C	A	C	C	A	4

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Heptaborate

The $[B_7O_9(OH)_5]^{2-}$ anion is related to $[B_6O_7(OH)_6]^{2-}$ by condensing two *exo* OHs with a $B(OH)_3$ unit, forming an additional 6-membered ring (Figure 1b). It has a Christ and Clark descriptor of 7:4Δ + 3T.[7] An IHB is formed between the *exo*-OH and either O atom situated on the new ring (Figure 2b), giving rise to similar energies for all rotamers (Table 2). The weaker nature of the IHB ($r_{O\text{-}H}$ = 0.962 Å; $r_{O\cdots H}$ = 2.59 Å; $\angle_{O\text{-}H\cdots O}$ = 128.3 °; $r_{O\cdots O}$ = 3.27 Å) is highlighted in the low (< 0.01 a.u.) ρ_{BCP} value together with a much shorter BCP-RCP distance (almost to the point of BCP/NCP coalescence). A small (*ca.* 0.002 a.u.) reduction in ρ_{BCP}, together with a *ca.* 20 cm^{-1} red shift in ν_{OH} and negligible (< 0.001 Å) elongation in r_{OH} for *exo* vs planar hydroxyl groups confirms the weaker nature of the IHB. Rotation of the planar hydroxyl groups attached to trigonal boron atoms again have a negligible energetic effect due to absence of hydrogen bonding.

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